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REF-CITED:

U.S. PATENT DOCUMENTS

PAT-NO		ISSUE-DATE	PATENTEE-NAME
US-CL			
2697652		December 1954	Ribble et al.
23/260	N/A	N/A	
2955917		October 1960	Roberts et al.
423/392	N/A	N/A	
3715887		February 1973	Weatherly et al.
60/650	N/A	N/A	

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ABSTRACT:

In the operation of a nitric acid plant, the rate of flow of process air to
the converter in which ammonia is oxidized is controlled by injection of steam
at regulated rates into the heated tail gas from the nitric acid production,
thereby utilizing regulated mass flow power augmentation in the gas used for
powering the expansion turbines employed in driving the compressors operated to
furnish required process air at superatmospheric pressure to the nitric acid
plant.

2 Claims, 2 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 1

BRIEF SUMMARY:

(1) BACKGROUND OF THE INVENTION

(2) In the conventional commercial process for the manufacture of nitric acid
ammonia is oxidized by contact with air at elevated temperature over noble
metal catalyst to form initially nitrogen oxide, which in the presence of excess oxygen is further oxidized to nitrogen dioxide or its dimer. The (NO.sub.2).sub.x is absorbed in water to produce nitric acid as illustrated by
the equation:

(1) 3 NO.sub.2 + H.sub.2 O .fwdarw. 2 HNO.sub.3 + NO (A)

(3) The nitrogen oxide thus rleased is reoxidized to NO.sub.2 by contact with
so called "bleach" air introduced into the absorber.

(4) In the modern practice such plants are operated at superatmospheric
pressure of seven atmospheres or higher to take advantage of increased
oxidation rate of NO to NO.sub.2. The history of the development of the
pressure process thus far described and the reaction mechanisms involved as
well as certain of the calculations entering into the design of plants of this
kind are reviewed in a monograph by T. H. Chilton, entitled "The Manufacture of
Nitric Acid by the Oxidation of Ammonia"; Chemical Engineering

Progress
Monograph Series, No. 3, Vol. 56 (1969).

(5) Since the several progresive reactions involved in the conversion of
NH.sub.3 to HNO.sub.3 are exothermic the energy thus liberated is utilized to
supply at least part of the power for compressing the air to the desired operating pressure. In a conventional commercial system, the tail gas from the
absorber is reheated to the required temperature for operation of the expansion
turbine system furnishing power for driving the air compressors.

(6) With the application of stricter standards on fume abatement and to
protect the turbine blades from corrosion by the tail gas, it has been the
practice to purify the gas prior to introducing the same into the turbines or
discharging to the atmosphere. This can be accomplished by passing the
preheated tail gas over a noble metal catalyst in the presence of a reductant,
such as a hydrocarbn fuel, which reduces the NO.sub.x in the tail gas to
innocuous elemental nitrogen while residual oxygen in the gas stream is
consumed by combustion of the hydrocarbons to form CO.sub.2 and water. Since
additional sensible heat is thus released in the NO.sub.x abatement unit, the
additional energy thus made available is beneficially utilized in supplying
power for operation of the gas expansion turbines.

(7) Although a substantial part of the thermal energy of the gas

employed in
driving the expansion turbine system is derived from exothermic process heat
released in the oxidation of ammonia to nitic acid and that released in the
catalytic NO.sub.x abatement unit, this heat content is generally insufficient
in itself to meet the net power requirements of the turbine system in modern
plants operating at superatmospheric pressure. Additional heat is generally
supplied by direct heating of the tail gas in a burner to which external fuel
is supplied together with air to support combustion. Such heating of the tail
gas, moreover, raises the temperature thereof to an efficient level for
promoting the catalytic reduction of the residual NO.sub.x in the abatement
unit.

(8) As seen from the foregoing description, the air compressors driven by the
expansion turbines supply air at superatmospheric pressure utilized in the
nitric acid plant. The stream of compressed air thus supplied may be divided
into three individual branch streams, providing (1) reactant air furnishing
oxygen for initial reaction with ammonia in the converter, (2) bleach air for
oxidation of NO in the absorber, and (3) air utilized to support combustion in
the direct fired heater.

(9) To obtain the desired high nitric acid production rates at maximum
efficiency, it is important not only that the flow of air and ammonia to

the
converter for the initial oxidation reaction be regulated but also that controls be maintained on the total air supplied to the system by the compressors. Even though a plant may have been initially designed for
appropriate flow rates and system power balance, unintended variations in air
flow which may result from changes in pressure and/or temperature of the
incoming air supplied to the compressors, or intentional changes in production
schedules will necessitate adjustment of the several components of the system
to satisfy the new conditions imposed. Because of the interdependent relationships of the various components of the system, it will be appreciated
that even small changes in any one of these, unless properly compensated, will
throw the whole system out of balance and may "snowball" the effect of such
change with consequent deleterious influence on the efficiency and economics of
the plant operation.

(10) Various concepts have been suggested or attempted for monitoring and
controlling nitric acid plant operation, none of which have been found fully
satisfactory to obtain the desired objectives. In modern plants a constant
ratio of air to ammonia introduced into the oxidation converter is automatically maintained by provision of ratio set stations responsive to
measured variations in air flow rate. To maintain the designed production
rate, however, the flow of air to the ammonia converter must also be set and

maintained substantially constant despite possible variation in the flow rate of air discharged by the compressor system. In preliminary studies leading to the present invention, it was found that in attempting to manipulate the firing rate in the direct fired heater to provide a controlled steady supply of air at the compressor outlet, there was a massive thermal inertial lag between the point at which the firing rate was changed and the point at which the effect of such change is ultimately felt.

(11) BRIEF STATEMENT OF THE INVENTION

(12) Among the objects of the present inention, therefore, is to provide an efficient and reliable control system for operation of nitric acid plants, which can be readily adapted for automatic operation.

(13) In principle, the novel control system of the present invention entails a mass flow power augmentation method as opposed to a heat supply method of operational control, thus avoiding the thermal inertia lag characteristic of the latter method.

(14) Succinctly stated, in accordance with the present invention, the rate of flow of process air to the ammonia converter is controlled by regulated injection of steam into the direct fired heater, while the firing rate in that heater is controlled to maintain a preset temperature for the gas mixture

discharged from the heater. The rate of supply of hydrocarbon fuel to the NO.sub.x abatement combuster unit is maintained by suitable controls at a set ratio to the gas flow rate of absorber tail gas into the direct fired heater.

(15) The operation of the invention will be fully understood and its several advantages appreciated from the detailed description which follows read in connection with the accompanying drawings illustrating a preferred embodiment thereof.

DRAWING DESCRIPTION:

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a schematic process flow diagram of a nitric acid plant to which the novel control system of the present invention may be applied; and

FIG. 2 is a further simplified flow diagram illustrating the control stations and their interrelation utilizing the novel system of the present invention.

DETAILED DESCRIPTION:

(1) DETAILED DESCRIPTION OF THE PROCESS

(2) As shown in FIG. 1, an air stream at ambient conditions is admitted to a three stage compressor system, generally designated 2, comprising compressor

units mechanically coupled to be driven by associated gas expansion turbine
units. The compressor system illustrated comprises in the first stage a
compressor 3 coupled to and driven by a turbine 4. The air thus compressed is
discharged through line 5, passed through interstage cooler 6 into second stage
compressor 7 in which it is further raised in pressure. Compressor 7 is
coupled to and driven by expansion gas turbine 8. The compressed gas
discharged from 7 passes through interstage cooler 9 into final stage compressor 10, driven by gas turbine 11. From the last stage of compression at
10, the process air stream 14 is discharged at the design pressure, usually in
the range of about 7 to 10 atmosphere absolute.

(3) While in the embodiment described and illustrated, a three stage compressor-expander-system is referred to, it will be understood that the
invention is in no way limited to such system, and is equally applicable to
systems having a greater or lesser number of compression stages. Moreover, any
compression stage may comprise two or more compressor - expander units
operating in parallel. Such a system for use in a nitric acid plant is described in Weatherly et al U.S. Pat. No. 3,715,887 which may be used in
practice of the present invention. Although the process gas usually employed
in nitric acid plants is atmosphere air, it will be understood that the air supply may be enriched with supplemental oxygen supplied from an external
source, and the novel control system of the invention is equally

applicable
thereto.

(4) Air stream 14, as illustrated, is subdivided into several branch streams designated 15, 16, and 17, respectively. Stream 15 furnishes the air used in oxidation of ammonia. Thus, stream 15 is admixed with ammonia introduced by line 18 into catalytic converter 20, in which the initial oxidation takes place over known noble metal catalyst, forming oxides of nitrogen, chiefly NO. The gas stream of reaction products from converter 20 is passed through a waste heat boiler 21 in which the stream is initially cooled, and then through a heat exchanger 22 and cooling condensor 23, for further lowering of the temperature prior to admission of the thus cooled gas stream in absorber tower 24.

(5) Water is admitted to absorber 24 by a supply line 25. As the NO-containing gas stream is successively cooled at 21, 22 and 23 in the presence of excess oxygen, at least the major portion of the NO is converted to NO.sub.2, in accordance with the equation

(1) 2NO + O.sub.2 .revreaction. 2NO.sub.2 (B)

(6) by the absorption of the NO.sub.2 in water in absorber 24, nitric acid (HNO.sub.3) is formed as illustrated by equation (A) above with release of NO as by product in the absorber. So called "bleach air" is charged to the bottom of absorber 24, by line 16, which effcts oxidation of NO to NO.sub.2,

which in
turn is reactively absorbed in the water to form additional nitric acid. The
aqueous nitric acid solution is discharged from absorber 24 by line 26, while
the unabsorbed tail gas is discharged overhead by line 27.

(7) The discharged tail gas passes through a preheater 28 for indirect heat
exchange with steam and then further raised in temperature in exchanger 22 by
hot product gas from 20 and 21. The tail gas thus pre-heated passed by line 30
to a direct fired heater 31, for further temperature elevation. Fuel for
heater 31 is furnished by a line 23, while the oxygen needed for combustion
thereof is supplied to the heater by line 17. To increase available energy in
the products of combustion from heater 31, steam may be injected by line 33.

(8) The total effluent from heater 31, in addition to the added steam and
products of fuel combustion, will contain oxides of nitrogen (NO.sub.x) which
are deleterious both from the standpoint of their effect on the turbine parts
as well as their pollution on discharge to the atomsphere. It is therefore
common practice to convert these nitrogen oxides to innocuous gas by reduction
to elemental nitrogen. Such reductions of NO.sub.x in the gas stream
discharged from 31 is carried out by catalytic combustion in a NO.sub.x
abatement unit 35, wherein the gas is treated with a suitable reductant, such
as natural gas or other hydrocarbon fuel, admitted thereto by line 36.

If available and so desired, the reductant hydrocarbon fuel admitted to abatement unit 35, may be supplemented with hydrogen-containing off gas. Abatement unit 35 contains noble metal or other suitable catalyst promoting the desired reduction of NO.sub.x. In unit 35 also, remaining oxygen in the gas stream from heater 31 is consumed in combustion of the hydrocarbons and any free hydrogen to CO.sub.2 and water. As a result of the several reactions taking place in unit 35 the temperature of the gas is further increased, and is then discharged through line 37 into the expansion gas turbine 11 driving the third stage air compressor 10 of system 2. The discharge gas from turbine 11 passes successively through turbines 8 and 4, and is finally discharged to stack through line 40.

(9) The system thus far described is of a type which is for the most part in commercial nitric acid plants. The novel monitoring and control features subject of the present invention, will now be described as applied to a plant of the type illustrated.

(10) The interrelation of the several control stations of the novel system of the invention will be understood from the simplified process flow diagram of FIG. 2. Like parts are numbered similarly to those in FIG. 1.

(11) The compressed gas from the third stage of compression is divided into
three branch streams as heretofore described, one (17) going to the direct
fired heater, one (16) to the absorber for use as bleach gas and the third (15)
going to the oxidation of ammonia. The rate of flow of air in line 15 is measured by any known suitable means indicated at 50, and the flow rate of
ammonia to be admixed therewith is proportionately set to maintain the desired
constant ratio of ammonia/air under control of flow controller 51 in ammonia
line 18. Thus any change in the flow rate of air in line 15 detected at 50 is
signalled to flow controller 51, which is designed to adjust the position of
valve 53 in the ammonia supply line, thereby to maintain the set fixed ratio of
ammonia to air entering convertor 20.

(12) The air flow rate in line 14 is determined by the operation of the compressor system under the influence of the energy input to the gas turbine
system driving these compressors. Variations in the temperature and/or the
mass flow rate of the driving gas supplied to the turbine system by line 37
will effect corresponding changes in the flow rate of air in line 14. The quantity of air employed as bleach air is set at a constant rate at valve 54 in
line 16. The supply of combustion air through line 17 is maintained at a fixed
predetermined ratio for combustion of the gaseous fuel supplied to heater 31
through line 32, under control of ratio setting device at 55. A temperature

sensing element 56 in line 34 carrying combustion products from heater 31 to
catalytic combustion unit 35, signals controller 57 and through a cascade
hookup energizes flow control device 58 to actuate the valve 59 in fuel line 32
in a direction to increase or decrease the fuel supplied to heater 31 as required to maintain the temperature set at 56.

(13) Since the amount of air withdrawn by line 17 for combustion is only a
small fraction of the total air supplied by line 14 (generally less than 5%),
the slight deviations in air flow in line 17 to satisfy that needed for combustion of the fuel supplied to maintain the desired temperature set at 56,
will have no important effect on the air flow measured at 50. Accordingly, the
flow rate of air in line 15 can be controlled by the mass flow rate of steam
admitted to heater 31 through line 33. Any deviations from the air flow rate
set at flow controller 52, as measured at 50, are transmitted through a cascade
hookup to flow controller 60, which in turn operates valve 61 to supply steam
at the rate required to restore the air flow rate at 50 to the preset design
value, since the amount of steam thus supplied controllably determines the
enthalpy of the gas and thus the energy input to the turbines by line 37.

(14) In heater 31, the tail gas in line 30 may be raised some 200.degree.-300.degree.F (.about.110.degree.-165.degree.C) above that at which
such gas enters the heater. Further increase in the temperature of

the gas to
that desired to power the gas turbines, is had in the catalytic combustor 35.
The quantity of fuel supplied to combustor 35 is controlled by valve 63 under
influence of flow controller 64, and is dependent upon the flow rate of tail
gas to heater 31. Thus, the flow rate measured in the line 30 is signalled
through appropriate hookup from flow indicator 65 to flow controller 64,
thereby actuating valve 63 to supply an amount of reductant fuel gas
proportional to the tail gas supply. In combustor 35 not only are NO and
NO.sub.2 reduced to elementary nitrogen but residual free oxygen in the tail
gas is also consumed by burning of the hydrocarbon to carbon dioxide and water.
In installations in which a hydrogen-containing off gas is used to supplement
part of the hydrocarbon fuel supplied to combustor 35, appropriate control
devices will be provided in line 49, to maintain the desired ratio of off-gas
to hydrocarbon fuel.

(15) A typical commercial nitric acid plant requires approximately in the
order of 9300-9400 s.c.f.m. of process air at a pressure above 120 psig and at
a temperature of about 270.degree.-290.degree.F for each 100 tons/day of nitric
acid produced (i.e. .about. 361 to 366 liters/hr air at above 9 atmospheres
absolute pressure at about 132.degree.-143.degree.C for each 90.7 metric tons
of nitric acid). The resulting tail gas will comprise about 34000

pounds/hr
(74,958 kg/hr) at about 7.5 atmospheres. For operation of the high temperature
high pressure expansion turbine driving the third or final stage compressor,
the tail gas is brought to a temperature of about 1200 .+-. 50.degree.C
(620.degree.-675.degree.C).

(16) While the foregoing description is concerned with control of a chemical
process system for manufacture of nitric acid, it will be understood that the
principle of the invention is applicable to any chemical manufacture system
employing compressed air as a process gas and having a significant amount of
tail gas which is or can be brought to a temperature and enthalpy sufficient to
provide at least a substantial part of the energy for powering gas expansion
turbines for driving the air compressors.

(17) In a system such as a nitric acid plant of the type described, sufficient steam will be available for injection into heater 31, by recovery of
exothermic heat from the ammonia oxidation reaction, for example that collected
from waste heat boiler 21. In studies conducted in a dynamic model of the
described system it was found that a steady steam injection rate into the
heater of about 150 lbs/min was required to obtain a turbine inlet gas temperature of 1150.degree.F (621.degree.C) and that for 1206.degree.F
(652.degree.C) turbine inlet temperature the steady steam injection rate was

102 lbs/min (46.27 kg/min). Plotting of experimental data over the temperature
range revealed the general guide rule that approximately 5% steam by weight of
tail gas entering the heater is required for a turbine gas inlet temperature of
about 1200.degree.F (.about. 649.degree.C). Lesser amounts of steam can be
employed at higher discharge temperature from heater 31 but at the expense of
increased fuel costs.

(18) Data from the dynamic model studies further revealed that, in runs in
which it was attempted to control the process air flow rate at the design level
by manipulation of the firing rate in the direct fired heater by varying the
rate of fuel supplied thereto, as the firing rate was increased in attempt to
provide an increased supply of air to the ammonia convertor, there was a larger
amount of air diverted to the direct fired heater to support combustion of the
higher fuel supply thereto, thus initially causing an undesired opposite effect
to that desired, in temporarily lowering the rate of air supplied to the
ammonia convertor, evidenced by a dip of the process air supply rate below its
starting rate. It was only after about two minutes elapsed that the effect of
the increased firing rate in the direct fired heater was felt in the process
air rate through increased turbine power input. In all cases at least 8 to 10
minutes was required to reach design flow. Several times this period would be

required to reach steady state conditions even if no additional upset were to
occur.

(19) In runs in which the novel arrangement of the present invention was
used, wherein steam injection was employed to control process air flow rate,
the effect of the control system was almost immediate without the dip or lag
earlier experienced, even under more severe tests in which the controls were
put into operation at the start. Design flow was reached in approximately one
minute with a fast controller setting, and stabilization at near the design
rate in two to three minutes.

CLAIMS:

What is claimed is:

1. In a system for operating a chemical plant utilizing compressed process
gas wherein the energy for compressing said gas is furnished at least in part
by the augmented enthalpy of a waste gas derived from such chemical plant, said
system including: gas compressor means driven by gas expansion turbine means,
first conduit means for conducting compressed air to a chemical processing
unit, second conduit means for conveying the discharged waste gas from said
chemical processing unit to said gas expansion turbine means, and means in the

path of said second conduit means in advance of said turbine to raise the
temperature and augment the enthalpy of said tail gas; the improved arrangement for monitoring and controlling the flow rate of the compressed
process gas supplied to said chemical processing unit, said arrangement
comprising:

a. a heater provided with an inlet for waste gas discharged from said
chemical processing unit and a discharge conduit for heated effluent gas;

b. a fuel gas supply line for introducing combustible fuel into said heater;

c. an air supply line for introducing air for supporting combustion in said
heater;

d. flow control means in (b),

e. flow control means in (c),

f. a temperature sensing means in the discharge conduit of said heater;
said sensing means being operatively connected to temperature control means
responsive thereto; said temperature controls means being effective in
manipulating the flow control means (d) to maintain a substantially constant
temperature at (f);

g. ratio control means operatively associated with said temperature control

means of (f) and said flow control means (e), to maintain a preset constant
ratio of air to fuel supplied to said heater;

h. a steam supply line communicating with said heater for injection of steam
therein;

i. flow control means on said steam supply line;

j. flow rate measuring means in the said first conduit conducting compressed
air to said chemical processing unit; and

k. means for signal communication between said flow measuring means (j) and
said flow control means (i), whereby said control means (i) is responsive to
variations in air flow rate measured at (j) to supply controlled quantities of
steam to the heater to augment the enthalpy of the gas powering said turbine
means, to the extent required to compensate deviation and to maintain the air
flow rate to the chemical processing unit substantially constant.

2. A nitric acid plant involving oxidation of ammonia vapor by oxygen-containing gas at superatmospheric pressure; said plant having an
ammonia oxidation convertor and an absorber for absorption of produced oxides
of nitrogen in liquid aqueous media, said absorber being provided with conduit
means for discharge of unabsorbed tail gas; said plant being further provided
with compressor means for compressing said oxygen-containing gas for

introduction into said converter, gas expansion turbines operatively connected
to said compressor means for driving the latter and means for heating the tail
gas discharged from said absorber; an inlet conduit for introduction of tail
gas into said heater, a conduit for introduction of fuel gas into said heater,
a conduit for introduction of combustion supporting gas into said heater and a
steam line for injection of steam into said heater; a discharge line for
conveying heated gas from said heater to a catalytic combustion unit downstream
of said heater; said catalytic combustion unit being provided with a conduit
for introduction of reducing gas thereinto for reduction of residual oxides of
nitrogen to elemental gas, means for conducting hot gas from said catalytic
combustion unit to said expansion turbines, and a control system comprising:

a flow rate indicator measuring the rate of flow of oxygen-containing gas
into said converter, a flow controller on said steam line responsive to
deviations in gas flow rate from the value preset at said indicator; a
temperature sensor in the line from said heater to said catalytic combustion
unit, a temperature control device operatively connected to said temperature
sensor; flow control means in said fuel introduction conduit responsive to
said temperature control device adapted to maintain a substantially constant
temperature in the gas stream monitored by said temperature sensing device;
flow control means in said conduit supplying combustion supporting

gas to said
heater, said flow control means being responsive to a ratio control means to
maintain a preset ratio of combustion supporting gas to fuel introduced into
said heater; a flow measuring device on the inlet conduit conveying tail gas
to said heater, and a flow control device in said conduit for introduction of
reducing gas into said catalytic combustion unit, said last named flow control
device being responsive to the measured tail gas flow rate entering said heater
to maintain a preset ratio of reducing gas admitted to the catalytic combusion
unit to the flow rate of tail gas entering said heater.